Study of Electrical Transport Properties in Thermally Evaporated Cu$_2$S Thin Films

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Abstract

Cu$_2$S was synthesized by vacuum evaporation under a pressure of $10^{-6}$ torr at an evaporation rate of 3 Å/sec. The electrical properties of Cu$_2$S thin film were studied using current-voltage characteristics. The conductivity was found to exhibit two distinct mechanisms within the applied field i.e., low voltage region and high voltage region. The most probable conduction mechanism prevailing in Cu$_2$S thin film is found to be Poole-Frenkel effect. Activation energy has been calculated for different thicknesses and is found that activation energy decreases with increase in film thickness. Dielectric constant of the film was measured using impedance analyzer. Plot of dielectric constant vs. frequency shows normal dielectric behavior of the film. Photocurrent of Cu$_2$S film increases with increase in film thickness.

Key Words: I-V Characteristics, C-V Characteristics, Dielectric Effect, Photocurrent

1. Introduction

Copper sulphide being an II-VI compound is an important material from the point of basic research, because it is known to exist in several crystallographic and stoichiometric forms. The principal advantage of II-VI compounds for terrestrial solar photovoltaic are low cost and ease of deposition of good quality films from these materials by a variety of growth methods. Due to their high photosensitivity, high absorption coefficient and direct band gap these II-VI semiconductors are of great interest in electronic and opto-electronic devices. Copper sulphide film exhibit several crystalline forms and variety of orientation with respect to substrate depending on deposition parameters.

Copper sulphide is found to exist in two forms at room temperature as ‘copper-rich’ and ‘copper-poor’. Copper rich phases exist as chalcocite, djurlite, digenite and anilite [1] and copper poor phase are existing as coveellite. It is well established that Cu$_2$S is the optimum proportion for obtaining high efficiency solar cells with high stability against oxidation and degradation. Due to the presence of copper vacancies in the film, Cu$_2$S exhibit P-type conductivity and act as electron acceptors that give rise to free holes. Cu$_2$S (x = 1 to 2) thin films have numerous technological applications such as sensors [2], as thermo electric and photoelectric converters [3], as field emission and photoluminescence [4], as solar controller and solar radiation absorber [5] as thermo-electric cooling material [6] and in micro-electromechnical-systems (MEMS) devices. Much attention has been focused on thin film Cd$_2$/Cu$_2$S hetero-junction due to their great promise as low cost solar power converter owing to their high efficiency up to 9.1% with improved stability [7]. Cu$_2$S thin films have been prepared by various techniques such as spray pyrolysis [8], modified
chemical method [9], photochemical method [10], va-
cuum evaporation method [11], chemical bath deposi-
tion (CBD) and atomic layer deposition (ALD) method.
Investigation on current-voltage characteristics seems to
provide more adequate method for distinguishing be-
tween different mechanisms of charge transport in the
material. The purpose of the present work was therefore
to report the current-voltage characteristics and dielec-
tric properties of Cu₂S thin film as a function of film
thickness prepared by vacuum evaporation method.

2. Experimental

2.1 Film Formation and Characterization

Cu₂S thin films of different thicknesses were de-
posited onto properly cleaned glass substrate with the
help of hind high vacuum coating unit at vacuum, 10⁻⁶
torr. Initially glass substrates were thoroughly washed
with soap solution and then with distilled water. Next the
glass substrates were kept in ultrasonic agitator for 45
min to remove the impurities present in the substrate.
Pure (99.99%) copper sulphide powder was used as the
source material and high purity aluminum electrode was
vacuum evaporated onto cleaned glass substrate on which
the films were deposited. Molybdenum boats were used
as source heater and the glass substrate was mounted on
the holder with heating arrangement. Thicknesses of the
film were measured using quartz crystal monitor whereas
temperature was measured with the help of fine wire
chromel and alumel thermocouple. Substrate to source
distance was optimized to be at 18.1 cm inside the va-
cuum chamber. Rotary drive was employed to maintain
uniformity in film thickness. Constant rate of evapora-
tion 3 Å/sec were maintained throughout the sample
preparation.

Current-voltage characteristics of the Cu₂S thin films
were studied by employing digital micro ammeter in
series with the capacitor and the voltage source. All
studies were performed under vacuum of about 680 torr.
Current-voltage behavior was studied in the temperature
range 300–400 K and the temperature during measure-
ments was maintained using variable voltage transformer.

A copper constantan thermocouple was used for the tem-
perature measurements. A potential of 20 volts was ap-
plied using DC regulated power supply in series with the
digital voltmeter. Capacitance-voltage measurements were
made at room temperature using LCR meter (LCR 819,
G. W. Ltd., Taiwan). Capacitance dependence of bias
was studied by applying reverse bias (0-2 V) in the fre-
quency range 30 KHz to 100 KHz, where the internal
bias of the LCR meter was switched OFF and the ex-
ternal bias was switched ON. The most commonly used
technique for measuring resistivity is the four point
probe method. The arrangement consists of PID con-
trolled oven (model-PID-200 scientific equipment and
services, Roorkee, India) in combination with low cur-
cent source (model-LCS-01) and digital micro voltmeter
(model-DMV-001). Photo current was measured by tak-
ing silver paste as a contact electrode at 1 cm separation,
which was applied on the film surface. A halogen lamp
was used for white light and the intensity of light was
measured in mW/cm² by placing a surya-amp at the posi-
tion of the sample. The samples are kept in measurement
chamber and photocurrent was measured using micro
ammeter.

3. Results and Discussion

3.1 I-V Measurements

Different types of mechanism namely tunneling,
impurity conduction, space charge limited conduction,
Schottky emission and Poole-Frenkel conduction take
place in semiconductor films. Information about the con-
duction mechanism prevailing in the Cu₂S thin film is
obtained from the current-voltage characteristics of Cu₂S
thin films. Figure 1 shows the current-voltage character-
istics of Cu₂S thin films of 1000 Å thickness at different
temperatures. It is observed from the entire graph that
current voltage curve has two distinct regions, low volt-
age region and high voltage region. At low voltage re-
geon (I<sub>V</sub>), indicating that the current is controlled by
thermally generating carriers and leads to ohmic be-
havior [12,13]. Ohmic behavior exists as long as free
carrier density continues to be in thermal equilibrium.
Conduction in the high voltage region does not seem to be ohmic, where the slope value is greater than 1, and this occurs when the carrier density becomes greater than the thermal equilibrium [14] in which square law region \((I \propto V^2)\) is obtained. Hence it is inferred that the conduction mechanism in these films may be either Schottky or Poole-Frenkel. In the schottky mechanism electrons are transported by thermionic emission across metal-semiconductor interface i.e., when the potential barrier is sufficiently thick the current flowing through the semiconductor is limited, whereas in the poole-frenkel effect electrons are thermally emitted from traps to conduction band. As a result the columbic potential barrier is lowered by external field, thereby increasing the probability of electron that results in increase in flow of current through the semiconductor.

The conduction mechanisms in these films are mainly governed by the grain boundary defect states and the defect states which effectively act as trapping or recombination centers play an important role in the determination of conduction mechanism in these films. Current-voltage relation according to Poole-Frenkel or Schottky has the form [15].

\[
I = I_o \exp(\beta E^{1/2}) / K_B T
\]  

where \(E\) is the electric field, \(\beta\) is the field lowering co-efficient, \(I\) is the applied current, \(K_B\) is the Boltzmann constant. The constant \(\beta\) is given by

\[
\beta = \sqrt{\frac{e^2}{\alpha \pi \varepsilon \varepsilon_0}}
\]  

where \(e\) is the charge of the electron, \(\varepsilon\) is the relative dielectric constant, \(\varepsilon_0\) is the permittivity of free space, \(\alpha\) is constant equal to 1 or 4 for Poole-Frenkel or Schottky effect respectively. In order to investigate the conduction mechanism prevailing in Cu2S thin film, the samples are subjected to high electric field between \(\ln I\) and \(E^{1/2}\) and the values of field lowering coefficient \((\beta_{exp})\) were calculated using the slope value in equation (1). Figure 2 shows the variation of \(\ln\) current with square root of applied field for Cu2S thin film of 1000 Å thickness. Table 1 shows the calculated Poole-Frenkel co-efficient value of 1000 Å thickness and the values found to be in the range \(1.07 \times 10^{-5} \text{ (mV)}^{1/2}\) to \(1.99 \times 10^{-5} \text{ (mV)}^{1/2}\) for the temperature \(303–403\) K. The calculated values \((\beta_{exp})\) are compared with theoretical value \((\beta_{theory})\) and evidently it is found that the experimental value of ‘\(\beta\)’ lie very near to the theoretical value of Poole-Frenkel co-efficient \((\beta_{pf})\) that was calculated using equation (2). Thus the conduction mechanism in Cu2S thin film is most probably be the Poole-Frenkel mechanism.

**Figure 1.** Variation of current with voltage measured at different temperature for Cu2S film of 1000 Å thickness.

**Figure 2.** Variation of current vs. square root of applied field measured at different temperature for Cu2S film of 1000 Å thickness.
effect based on the results obtained. It is observed that the curve exhibit linear current field characteristics at higher temperatures and within the ambient temperature range (323–343 K) the Poole-Frenkel co-efficient decreases as the temperature increases from (30 to 100 °C).

A condition for impurity conduction is the presence of donors, acceptors, structural traps and there are so many of these that dominate the conduction processes. When the traps are in abundance and a trap having a columbic type barrier would experience Poole-Frenkel effect at higher fields and acts as insulator. Further to confirm Poole-Frenkel mechanism in Cu2S thin film the dielectric constant $\varepsilon_r$ that has been determined using equation (2) and is listed in Table 1 along with the high frequency values of $\varepsilon_r$ obtained from equation (9). It is clear from Table 1 that the values of $\varepsilon_r$ obtained from capacitance measurement are in close agreement with the values obtained from $\beta_{pf}$ in Cu2S thin film.

Trap depth ($E_t$) for different voltages and film thickness of Cu2S thin film are calculated from the plot of log current versus inverse of absolute temperature (Figure 3) and using the slope value in equation (3) the calculated values are found to be in the range (0.2 to 0.09) eV for Cu2S thin film.

$$I = I_o \frac{\exp(-E_t)}{K_B T}$$

where $K_B$ is the Boltzmann constant, $T$ is the absolute temperature. From Table 2 it is evident that trap depth decreases with increase in applied voltage, indicating that the trap depth has been lowered in the presence of applied field [16]. The reason is that conduction band is lowered and hence the probability of electron [17] escaping from the trap increases and thereby reduces trap depth. Moreover, trap depth decreases with increase in film thickness which is due to decrease in inter-grain boundary defect states and thereby reduces trap depth [18].

Figure 4 shows the variation of trap depth with applied voltage for Cu2S thin film of different thickness

### Table 1. Experimental and theoretical values of $\beta$ for Cu2S film

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Experimental field lowering coefficient $\beta \times 10^{-5} \text{ (mV)}^{1/2}$</th>
<th>Theoretical field lowering coefficient $\beta \times 10^{-5} \text{ (mV)}^{1/2}$</th>
<th>$\varepsilon_r$ from capacitance measure</th>
<th>$\varepsilon_r$ from $\beta_{pf}$ measure</th>
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<tbody>
<tr>
<td>303</td>
<td>1.07</td>
<td>1.51</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>323</td>
<td>1.78</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>343</td>
<td>1.35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>1.79</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>403</td>
<td>1.99</td>
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</table>

### Table 2. Variation of trap depth with applied voltage

<table>
<thead>
<tr>
<th>Bias applied (volts)</th>
<th>Trap depth $E_t$ (eV) for different thicknesses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000 Å</td>
</tr>
<tr>
<td>2</td>
<td>0.197</td>
</tr>
<tr>
<td>4</td>
<td>0.118</td>
</tr>
<tr>
<td>6</td>
<td>0.112</td>
</tr>
<tr>
<td>$\Delta E_0$</td>
<td>0.30</td>
</tr>
</tbody>
</table>
and the intercept at $V = 0$ yields trap depth at zero field. The calculated value shows that at higher bias region the values almost remain constant, i.e., under increased bias the distance of the trap around the Fermi level to the top of valence band remain nearly constant.

3.2 C-V Measurements

Figure 5 shows the frequency dispersion of capacitance of Cu$_2$S films for two different voltages. From the plot it is observed that low frequency has high capacitance value and this may be attributed to the significant polarization of charge carriers that give rise to ionic conduction. The dipoles cannot orient themselves at higher frequencies and hence the capacitance decreases [19]. Moreover at higher frequencies the frequency dispersion of capacitance was almost constant.

The number of states can be calculated from the measured capacitance at low and high frequencies, where the capacitance at lower frequency is associated with depletion layer and interface states, whereas capacitance at higher frequency is associated with depletion layer only. The total number of interface states can be calculated using the relation.

$$N_{IS} = \frac{(C_{LF} - C_{HF})}{q}$$  \hspace{1cm} (4)

where $N_{IS}$ is the total number of interfaces states, $C_{LF}$ and $C_{HF}$ are the capacitance at lower and higher frequencies respectively and $q$ is the charge of an electron. Thus the total number of interface states ($N_{IS}$) calculated at low (70 kHz) and high frequencies (100 kHz) using equation (4) was found to be $1.8 \times 10^{17}$ for 1000 Å thickness.

The ionized donor density ($N_D$) was calculated from the slope of $1/C^2$ vs. bias voltage curve (Figure 6) known as (Mott-Schottky plot) [20,21] at $V_B$ close to zero and using the slope value in equation (5).

$$\frac{1}{C^2} = \frac{2(V_D + V)}{q\varepsilon_0 \varepsilon_A A^2 N_D}$$  \hspace{1cm} (5)

where $A$ is the area of the electrode, $\varepsilon_0$ the permittivity
of free space, $\varepsilon$ the dielectric constant of the material. Thus donor density ($N_d$) calculated from the above equation is found to be $5.57 \times 10^{16}/\text{cm}^3$. A negative voltage shifts in the frequency indicates the presence of positive charge carriers in the film [22]. The extrapolated value of voltage at $1/C^2 = 0$ gives the value of flat band potential as 2.4 V for 1000 Å thickness [17].

Barrier height ($\phi_B$) of the material can be calculated using the relation

$$\phi_B = V_f + V_n + \left(\frac{kT}{q}\right) - \Delta\phi$$

(6)

where $V_f$ is the voltage intercept, and $V_n$ is the depth of the Fermi level below conduction band. Barrier height thus calculated is seen to be 0.300 eV for 1000 Å thickness and is in good agreement with earlier reports of Cu$_2$S film [2]. It is also observed that barrier height decreases with increase in film thickness and the values found to be 0.100 eV for 7000 Å thickness. Thus it is concluded that higher thickness Cu$_2$S film have low barrier height and vice-versa.

### 3.3 Resistivity Measurements

According to the modern quantum electronic theory, electrical conduction in metals is due to electrons, while electrical resistivity results from the scattering of electrons by the lattice, therefore resistivity is the measure of metal lattice displacement from prefect regularity [23]. Figure 7 represents the variation of resistivity with inverse of absolute temperature for various currents (30–90 $\mu$A) of 7000 Å thickness. It is observed that resistivity initially decreases with temperature and attains a minimum value called as transition temperature and further increases with temperature. The transition temperature is estimated within (383–443 K) for 7000 Å thickness. These observations show that the material behaves as semi conducting nature at lower temperature and metallic above transition temperature [9,24] which is in good agreement with the earlier reports reported for Cu$_2$S thin film.

Figure 8 shows the variation of resistivity with temperature of Cu$_2$S sample for different thickness at constant current ($I = 50 \mu$A). The resistivity of the film is seen to increase with increase in film thickness and this increase in resistivity is due to surface of the film, which is covered with circular islands with lot of empty spaces between them producing number of grain boundaries and hence results in increase in resistivity [25]. The grain size of the film is determined by using the Scherrer formula [2]

$$d = \frac{0.9\lambda}{\beta\cos\theta}$$

(7)

where $\lambda$ is the wavelength used, $\beta$ is the angular line

![Figure 7. Variation of resistivity vs. inverse of temperature for Cu$_2$S film of 7000 Å thickness.](image1)

![Figure 8. Variation of resistivity vs. inverse of temperature for Cu$_2$S of different thickness.](image2)
width at half maximum, $\theta$ is the Bragg’s angle and the values are reported in Table 3. From Table 3 it is evident that the grain size decreases with increase in film thickness, which is due to the presence of new grains over older ones. Again it is seen from the graph that the resistivity decreases for the film coated at higher thickness, which is due to increase in grain size of the film at higher thickness and have opposite effect [26] (Table 3). The reason for the sudden decrease in resistivity of the film is that these islands continue to grow into bigger grains showing overgrowth on the film surface.

Activation energy ($E_0$) for different thicknesses of Cu$_2$S sample are calculated from Figure 8 and using the slope value in equation (8) the calculated values are entered in Table 4.

$$\rho = \rho_0 \frac{\exp(-E_0)}{K_BT}$$  \hspace{1cm} (8)

Figure 9 shows the variation of log resistivity verses inverse of absolute temperature curve for 5600 Å film thickness at constant current ($I = 50 \mu A$). It is inferred from Table 4 that activation energy decreases with increases in film thickness and this may be due to the presence of defect states in the film.

### 3.4 Dielectric Measurements

The Poole-Frenkel effect is often observed in dielectrics and in amorphous materials due to the presence of large number of defect states in the energy gap of the material. The dielectric constant ($\varepsilon_r$) of the material in the frequency range (10–100 Hz) was calculated using the formula.

$$\varepsilon_r = \frac{Cd}{A\varepsilon_0}$$ \hspace{1cm} (9)

where $C$ is the capacitance of the film, $A$ is the area of the electrode, $d$ is the thickness of the film and $\varepsilon_0$ is the electrical constant. Variation of dielectric constant as a function of frequency for different thickness is shown in Figure 10. The larger dielectric constant value of Cu$_2$S thin film is due to the fact that the particles act as dipoles under the influence of electric field. As the par-

<table>
<thead>
<tr>
<th>Thickness (Å)</th>
<th>Grain size (nm)</th>
</tr>
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<tbody>
<tr>
<td>1000</td>
<td>207.59</td>
</tr>
<tr>
<td>3500</td>
<td>138.40</td>
</tr>
<tr>
<td>5000</td>
<td>19.77</td>
</tr>
<tr>
<td>7000</td>
<td>103.79</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Thickness (Å)</th>
<th>Activation energy $E_0$ (eV)</th>
</tr>
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<tbody>
<tr>
<td>1000</td>
<td>0.595</td>
</tr>
<tr>
<td>5000</td>
<td>0.525</td>
</tr>
<tr>
<td>7000</td>
<td>0.450</td>
</tr>
</tbody>
</table>
article size is in nanometer range, the number of particles per unit volume is very large and hence the dipole moment per unit volume increases, so the dielectric constant increases. Again it can be seen from the figure that dielectric constant increases with increase in thickness which is due to the decrease in size of the particle at higher thickness (Table 3). Due to this reason the number of particle per unit volume increases and hence the dielectric constant increases [27]. Dielectric losses are generally reflected in resistivity measurements i.e., materials with high resistivity exhibits low dielectric loss and vice-versa [28]. Therefore it is concluded that low thickness Cu₂S film exhibiting high resistivity has low dielectric loss when compared to higher thickness film.

3.5 Photocurrent Measurements

When the film is illuminated by light, additional photo excited carriers are generated in the films. As a result, part of thermally excited carrier together with large number of photo-generated carriers neutralizes some fraction of localized charges in the depletion regions in the grain boundary potential barriers. Photoconductivity signal versus intensity of incident light is described by the relation [29]

\[ I_{pc} \propto (I_L)^\alpha \]  

(10)

where \( I_{pc} \) is photo current, \( I_L \) is the incident photon flux and \( \alpha \) is the empirical constant. The variations of photo current with applied voltage for different film thickness are shown in Figure 11. The conductivity is found to increase exponentially with applied voltage [18,30] as well as film thickness. It is observed form the graph that the film exhibit linear dependence of photocurrent with applied voltage and this behavior indicates that the film is free from trap.

4. Conclusion

The conduction mechanism in evaporated Cu₂S thin films was analyzed from the current-voltage characteristics. The possible conduction mechanism in Cu₂S films is found to be Poole-Frenkel type. The ionized donor density, flat band potential, barrier height are calculated form the capacitance voltage measurements. Resistivity studies revealed that low temperature Cu₂S thin films exhibit high conductance while high temperature film has high resistance. Higher thickness Cu₂S films with low resistivity and low barrier height has superior conducting behavior than low thickness Cu₂S films. The Cu₂S thin films exhibit high dielectric value and this dielectric increases with increase in film thickness.

References

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Manuscript Received: Aug. 10, 2011
Accepted: Mar. 13, 2012